

(12) **UK Patent Application** (19) **GB** (11) **2 138 430 A**

(43) Application published 24 Oct 1984

<p>(21) Application No 8409834</p> <p>(22) Date of filing 16 Apr 1984</p> <p>(30) Priority data (31) 486485 (32) 19 Apr 1983 (33) US</p>	<p>(51) INT CL³ C08J 3/20 5/04</p> <p>(52) Domestic classification C3L DH C3W 100 202 203 208 213</p> <p>(56) Documents cited GB A 2071112 GB 1447625 GB 1269536 GB 1514827 GB 1277808 GB 1046811</p> <p>(58) Field of search C3L</p>
<p>(71) Applicant Polysar Limited (Canada), Sarnia, Ontario, Canada N7T 7M2</p> <p>(72) Inventors Douglas Cameron Edwards James Alan Crossman</p> <p>(74) Agent and/or Address for Service Gill Jennings & Every, 53/64 Chancery Lane, London WC2A 1HN</p>	

(54) **Mixing polymers and fibrous materials**

(57) A process for the production of a mixture of a polymer and a fibrous material, which comprises agitating an aqueous solution of a coagulant for the polymer; adding an aqueous suspension of the fibrous material to the coagulant solution; adding the polymer, in aqueous latex form, to the coagulant solution; co-coagulating the polymer and the fibrous material; and recovering and drying the mixture of polymer and fibrous material. Mixtures produced by this process can be vulcanised.

GB 2 138 430 A

SPECIFICATION

Mixing polymers and fibrous materials

- 5 The present invention relates to a process for the production of a mixture of a polymer and a fibrous material, and to a process for vulcanising such a mixture. 5
- A great variety of fillers (usually considered non-reinforcing) and/or reinforcing materials, for plastics and for rubbers, is known. Fillers are usually particulate inorganic compounds. Common reinforcing materials are particulate carbon blacks and certain particulate inorganic compounds.
- 10 Fibrous materials are frequently added to rubber compounds, to improve various properties and to reduce the extent of fabric reinforcement. Suitable such fibres include asbestos, cellulose, glass, cotton and various synthetic organic fibres such as polyester and rayon. The fibre may be used as short, for example, chopped, fibres, or as longer fibres. An important aspect of the use of such fibres is the incorporation into the polymer matrix. 10
- 15 US-A-1991367, US-A-2419512 and US-A-2441090 are examples of disclosures that carbon black may be incorporated into polymers by mixing, particularly as a suspension in water, with a polymer in latex form, and coagulating the mixture. US-A-4263184 discloses a homogeneous pre-dispersed fibre composition prepared by mixing a latex of a polymer with fibrous material, to form a wetted fibre mixture, and then mixing a coagulant with the wetted fibre mixture. 15
- 20 According to the present invention, a process for the production of a mixture of a polymer and a fibrous material comprises agitating an aqueous solution of a coagulant for the polymer; adding an aqueous suspension of the fibrous material to the coagulant solution; adding the polymer, in aqueous latex form, to the coagulant solution; co-agulating the polymer and the fibrous material; and recovering and drying the mixture of polymer and fibrous material. 20
- 25 A vulcanisation process according to the invention comprises mixing, shaping and vulcanising, at elevated temperature, a mixture of polymer and fibrous material produced by a process according to this invention, rubber-compounding ingredients and vulcanisation-active agents. 25
- The polymer may be natural rubber or, preferably, a synthetic rubbery polymer. Examples of synthetic rubbery polymers normally produced by emulsion polymerisation, and available in the latex form, are styrene-butadiene, butadiene-acrylonitrile, carboxylated styrene-butadiene and carboxylated butadiene-acrylonitrile polymers, polymers comprising chloroprene, and polymers comprising acrylic monomers. Other synthetic rubbery polymers in latex form are butyl rubber, halogenated butyl rubber, polybutadiene and ethylene-propylene-non-conjugated diene polymers. Preferred among these polymers are styrene-butadiene polymers having an average
- 30 styrene content of from 15 to 40% by weight, mixtures of two or more styrene-butadiene polymers, in which the average styrene content is from 45 to 60% by weight, carboxylated styrene-butadiene polymers having a styrene content of from 15 to 40% by weight and a bound carboxylic acid monomer content of from 2 to 10% by weight, butadiene-acrylonitrile polymers having an acrylonitrile content of from 20 to 50% by weight, carboxylated butadieneacrylonitrile 30
- 40 polymers having an acrylonitrile content of from 25 to 40% by weight and a bound carboxylic acid monomer content of from 2 to 10% by weight, and polymers comprising chloroprene. Such preferred polymers may also contain a compatible extender oil or plasticiser, such as hydrocarbon oils for the styrene-butadiene polymers and alkyl esters for the butadiene-acrylonitrile polymers and polymers comprising chloroprene. 35
- 45 The fibrous material used in this invention may comprise or consist of cellulosic fibres such as cellulose, modified cellulose, cotton, jute, wood pulp or sisal fibres, mineral fibres such as asbestos or mineral wool fibres, synthetic inorganic fibres such as glass fibres or glass yarn, and synthetic fibres such as rayon, nylon, polyester, polypropylene or aramid fibres. Preferred fibrous materials include fibres that are fibrillated, especially those which contain numerous fine 45
- 50 diameter fibrils attached to the main fibre. An especially preferred fibrous material is a polymeric paraphenylene terephthalamide aramid having an average fibre length of from 1 to 5 mm and a BET surface area greater than 1 m²/g. Preferably, such aramid fibres are used in the wet pulp form, and their BET surface area is from 7 to 12 m²/g. Satisfactory results have been achieved using fibres of the polymeric paraphenylene terephthalamide known as KELVAR (RTM) having a 50
- 55 surface area greater than 1 m²/g. The preferred KEVLAR in the form known as wet pulp has a fibre length of from about 1 to about 5 mm, preferably from about 2 to about 4 mm, has a BET surface area of from about 7 to about 12 m²/g and contains from about 40 to about 60 weight percent of water. Examples of wet pulp have been described by duPont as merge 6F104 and F205 and as having Canadian Standard Freeness, respectively, of 450 to 575 and 300 to 425. 55
- 60 Such fibrous material may be mixed with water and readily forms very thick suspensions of high viscosity even at concentrations of only about 2 weight per cent in water. If the fibrous material is dried to remove the residual water associated with the wet pulp, it has been found that it is impossible to form a uniform mixture (using any of the conventional polymer mixing equipment) of the fibrous material with any of the polymers described above under conditions regarded as 60
- 65 practical by those skilled in the art. The fibres do not disperse evenly in the polymer and occur 65

as agglomeration of fibre within a polymer matrix.

The coagulants used in the process of this invention are those well known in the art for the coagulation of the polymers from the latex. Suitable coagulants include the aqueous solutions of calcium chloride, sulphuric acid, sulphuric acid plus sodium chloride, sulphuric acid plus sodium chloride plus a polyamine compound as exemplified in Canadian Patent 979,595, sulphuric acid plus polyamine compound, alum, alum plus sulphuric acid, polyaluminium chloride also known as aluminium polyhydroxychloride, magnesium sulphate and the like. Selection of a suitable coagulant for use to coagulate any particular polymer from the latex is readily known to one of average skill in the art. For example, to coagulate a styrene-butadiene polymer from the latex, one may use sulphuric acid, sulphuric acid plus salt, sulphuric acid plus salt plus polyamine compound or polyaluminum chloride, to coagulate a butadiene acrylonitrile polymer from the latex, one may use calcium chloride or polyaluminum chloride and to coagulate polymers comprising chloroprene from the latex, one may use the polyvalent inorganic salts including calcium salts and alum.

The process of the present invention requires that the polymer latex be added to an agitated aqueous solution of the coagulant which also contains fibrous material suspended in the coagulant solution. The aqueous solution of the coagulant which also contains fibrous material suspended therein is prepared by adding the fibre to the coagulant solution, preferably to produce a dilute dispersion containing not more than about 1 weight per cent of fibre in the coagulant solution, and to subject the dispersion of fibre in coagulant solution to agitation for a short period of time to improve the separation from one another of the fibres before the polymer is added. Such agitation may be accomplished by any known means especially such as to achieve preferably a high degree of shearing action and would be for a period of time of from a few seconds, such as 2 or 3 seconds, up to not more than about 30 to 40 seconds. The polymer latex is then added to the dispersion of fibre in coagulant solution while the dispersion is being subjected to simple agitation. The fibrous material may be present in the coagulant solution as the total amount of fibre to be used or may be added as a dispersion in coagulant solution to the coagulation mixture continuously or intermittently as the latex is being added to the coagulant solution. Thus, for a batch type coagulation, it may be preferable to add all the fibrous material to the coagulant solution before the polymer latex is added, whereas for a continuous type coagulation it may be preferable to add a dispersion of the fibrous material in coagulant solution continuously or intermittently to the coagulation mixture while the latex is being added provided that part of the fibrous material is present in the coagulant solution before the addition of latex is initiated.

The coagulation will generally be undertaken with the coagulant solution maintained at a temperature of from about 25° to about 80°C, preferably from about 40° to about 70°C. The coagulant solution will be continuously agitated in order to mix all the components together. For a continuous process, coagulant solution will generally be continuously added to the coagulation mixture at a rate sufficient to provide the required coagulation mixture at a rate sufficient to provide the required coagulation action and the co-coagulated polymer-fibrous material mixture will generally be removed continuously, such as by overflow from the vessel as a suspension in the aqueous phase of coagulated polymer-fibre particles.

The concentration of fibrous material in the mixture of polymer and fibrous material is from about 0.25 to about 100 parts by weight of fibrous material per 100 parts by weight of polymer. In one preferred embodiment, the concentration of fibrous material is from about 0.25 to about 20, most preferably from about 2 to about 12, parts by weight per 100 parts by weight of polymer. In a second preferred embodiment, the concentration of fibrous material is from about 25 to 100 parts by weight per 100 parts by weight of polymer. The polymer latex will usually have a polymer content of from about 10 to about 45 weight per cent of polymer based on the latex, preferably from about 15 to about 30 weight per cent of polymer. The coagulant solution will contain the normal concentrations of coagulants, that is from about 0.5 up to about 8 weight per cent, and acid concentrations, when used, will be such as to provide a pH of from about 2 to about 5. All flows of the various streams will be established to provide the required relative concentrations of components. The fibrous material is mixed with and suspended in water, which suspension is added to some or all of the aqueous coagulant solution. The concentration of fibrous material in the suspension in water is not important—it may range from about 0.1 up to about 5 per cent by weight provided that it is still a pumpable suspension. The concentration of fibrous material in the coagulant solution will generally be from about 0.1 to about 0.5 per cent by weight.

The co-coagulation product, that is the mixture of polymer and fibrous material, is separated from the aqueous phase such as by mechanical separation means or by filtration, may be washed with water, is recovered and the wet particles of polymer-fibrous material mixture are dried, such as in a hot air drier or in a dewatering-drying means.

The mixture of polymer and fibrous material may be used in many of the end-uses normal for the polymer itself—such as various automotive products, tires, mechanical goods and the like as

applicable for the particular type of polymer. For example, a KELVAR wet pulp-styrene-butadiene mixture may be used in various aspects of tire construction including, but not limited to, in the apex (which is the area above the bead wire sometimes referred to as filler or bead filler), as a carcass protecting layer under the tread and sidewall, as a sidewall component to improve cut and snag resistance and in the undertread (sometimes called the base) to provide improved cut resistance especially for on/off road use in agricultural and such tires. The mixture of polymer and fibrous material may also be used in mixtures with one or more compatible polymers. Thus, for example, the mixture of polymer and fibrous material may be mixed with polymers not containing fibre to produce a final mixture containing a lesser content of fibrous material per one hundred parts of total polymers. To illustrate, a mixture of styrene-butadiene polymer and fibrous material may be mixed with a styrene-butadiene polymer containing no fibre and compounded in the usual manner, or a mixture of a polymer comprising chloroprene and fibrous material may be mixed with a polymer comprising chloroprene and containing no fibre and compounded in the usual manner, or a mixture of a butadiene-acrylonitrile polymer and fibrous material may be mixed with polyvinyl chloride containing no fibre and then compounded in the usual way, or a mixture of styrene-butadiene polymer and fibrous material may be mixed with one of or both of polybutadiene and natural rubber containing no fibre and compounded in the usual manner. In all such uses, the polymer-fibrous material mixture will be compounded in the usual way with rubber compounding ingredients, such as fillers, extenders or plasticizers, antioxidants or antiozonants and the like, and with vulcanization active agents using rubber mills or internal mixers. The compounded mixtures will be shaped and then vulcanized by maintaining at an elevated temperature for a period of time, such as by heating to about 140° to about 250°C for times of from about 5 minutes to about 2 hours.

Vulcanizates containing the polymer-fibrous material mixture of the invention possess improved properties when compared to vulcanizates of the same polymer containing no fibre. Such improved properties may include one or more of improved dimensional stability, increased modulus at low or moderate degrees of deformation and substantially increased resistance to tearing.

The following Examples illustrate the scope of the invention. All parts are parts by weight unless expressly shown otherwise. Tests used to evaluate the vulcanizate properties are ASTM tests adapted particularly for use with small samples of material. The fibrous material was used as provided and contained about 53 weight percent of water.

Example 1

A styrene-butadiene polymer (about 25 weight per cent of styrene) in latex form (about 22 percent solids) and an aramid fibre KEVLAR supplied as Wet Pulp having an average length of about 4 mm, merge number 6F104, Canadian Standard Freeness 450 to 575 and BET surface area of about 10 m²/g and supplied as a solid material containing about 53 percent of water, were used. The aramid fibre, as supplied, was added to water and subjected to vigorous agitation for about 5 minutes to provide a suspension of fibres in water with few, if any, agglomerations of fibre.

In Experiment 1, the fibre was suspended in water, mixed with the latex and the mixture maintained under agitation. A 1 percent solution of calcium chloride in water was slowly added to the mixture. This caused the formation of an agglomeration of at least part of the polymer and fibre which could not be adequately recovered. This experiment was a control. In Experiment 2, the latex was diluted with water (no fibre was added) and then added to a stirred 1% solution of calcium chloride—this led to the formation of an agglomeration of at least part of the polymer which could not be adequately recovered. This experiment was a control. In Experiment 3, the fibre was suspended in water and then mixed with 120 ml of 1% calcium chloride solution. The latex was added to the stirred mixture of fibre and calcium chloride which led to the formation of small particles of polymer and fibre which was readily recovered, washed with water and dried. Examination of the polymer-fibre mixture under a microscope showed it to be a uniform mixture of the components without significant agglomerations of fibre within the polymer. The details are provided in Table I.

TABLE I

Experiment		1	2	3
Weight of fibre	g	2.8	—	2.8
Volume of water	ml	200	300	300
Volume of latex	ml	200	200	200
Volume of calcium chloride solution	ml	—	120	120

Example 2

Using the materials described in Example 1, a further batch co-coagulation was conducted

similar to Experiment 3 thereof. 2.8 g of fibre were suspended in 300 ml of water which were then mixed with 120 ml of 1% calcium chloride solution. 200 ml of latex were slowly added to the stirred mixture of fibre and calcium chloride. The nature of the coagulating mixture was observed during the course of the latex addition and it was found that the polymer from the latex appeared to coagulate about the fibres, following which the polymer appeared to coagulate onto the surface of the so-formed particles.

Example 3

Continuous co-coagulations were undertaken using the latex and fibre of Example 1. A coagulation vessel was provided and equipped with an agitator and containing coagulant. A vessel was provided and equipped with an air-driven stirrer and an outlet flow control means to dispense controlled amounts of the fibre-water suspension to the coagulation vessel. A vessel equipped with an outlet flow control capable of providing a controlled flow of latex per unit time was used to supply latex to the coagulation vessel. For Experiments 4 and 5, the coagulant was a mixture of 900 ml of a 4% solution of sodium chloride in water and 75 ml of a coagulant solution which contained 443 g of sodium chloride and 17.6 g of concentrated sulphuric acid in 3540 g of distilled water. For Experiment 6, the coagulant was a solution containing 0.25 weight per cent of calcium chloride dissolved in distilled water. The fibre-in-water suspension contained for Experiment 4 1.4 g of fibre in 280 ml of water and was added in 9 ml aliquots over 13 minutes, for Experiment 5 1.4 g of fibre in 280 ml of water and was added in 9 ml aliquots over 6.5 minutes, and for Experiment 6 1.4 g of fibre in 280 ml of 0.2 weight per cent calcium chloride solution and was added in 9 ml aliquots over 13.5 minutes. For all the experiments, the first aliquot of fibre in water was added before the latex was added to the coagulation vessel. The latex was added to the coagulation vessel over 14.5 minutes for Experiment 4, 7.15 minutes for Experiment 5 and 15 minutes for Experiment 6. For Experiment 7, the procedure of Experiment 4 was followed except that 2.15 ml of naphthenic oil (ASTM D 2226, Type 103) was also added at the same time as the latex to the coagulation vessel over a time for both oil and latex of 15.25 minutes.

All coagulations produced small crumbs of coagulated polymer and fibre which were readily separated from the aqueous phase, washed and hot air dried to yield uniform mixtures containing essentially no agglomerations of fibre.

Example 4

Following the procedure of Example 2, further co-coagulations were undertaken to provide samples of polymer containing varying amounts of fibre. The fibre was added to a 1% solution of calcium chloride in water and the latex was added thereto with continuous agitation over a period of about 30 minutes. For Experiment 8, where no fibre was used, the coagulant was 2 g of calcium chloride dissolved in 400 ml of water. The coagulated polymers were recovered and hot air dried, yielding uniform dispersions of fibre in polymer. Portions of the polymer-fibre mixture were compounded, shaped into sheets, dumbbells cut for green strength measurements, the remaining sheets were vulcanized at 160°C for 10 minutes and dumbbells cut for vulcanizate property measurement. The compound recipe (based on 100 parts by weight of polymer) was 50 parts of carbon black, 3 parts of naphthenic oil, 3 parts of zinc oxide, 1.5 parts of stearic acid, 0.5 parts of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine, 0.5 parts of N,N'-bis(1,4-dimethylpentyl)-p-phenylene diamine, 0.3 parts of diphenylguanidine, 1.2 parts of N-tert.butyl-2-benzothiazole sulphenamide and 2 parts of sulphur. Further details are in Table II where for the green strength and vulcanizate properties W means with the grain and A means against the grain. The increase in green strength with increasing fibre content is readily seen. The increase in 100% modulus and trouser tear for the vulcanizates is readily seen.

TABLE II

Experiment		8	9	10	11	12	13	14	15	
Water	(ml)	400	300	300	300	400	400	450	500	
5 Calcium chloride	(ml)	(2g)	120	120	120	120	120	120	150	5
Fibre	(g)	—	2.8	5.6	8.4	11.2	14	16.8	19.6	
Latex	(ml)	200	200	200	200	200	200	200	200	
Fibre content of polymer-fibre mixture	phr	0	3	6	9	12	15	18	21	
10 Compound Green Strength										10
Max. Stress	(W) MPa	0.5	0.85	1.6	1.8	2.35	3.3	3.1	2.6	
	(A) MPa	0.5	0.6	0.7	0.8	1.0	1.1	0.8	0.8	
Elongation	(W) MPa	415	170	145	95	80	70	80	80	
	(A) MPa	370	180	200	140	70	80	90	90	
15 Vulcanizate Properties										15
100% Modulus	(W) MPa	2.4	6.4	9.0	11.1	13.7	14.7	—	—	
	(A) MPa	2.1	2.6	3.4	5.1	5.6	5.3	6.3	6.5	
300% Modulus	(W) MPa	14.3	15.3	16.0	13.5	17.0	—	—	—	
	(A) MPa	13.9	13.1	12.7	12.9	13.2	12.4	—	12.2	
20 Tensile Strength	(W) MPa	29.9	26.3	23.5	21.2	18.4	14.9	15.4	18.6	20
	(A) MPa	24.8	22.7	18.1	18.7	16.2	12.9	12.1	12.3	
Elongation	(W) %	490	430	410	390	320	110	50	40	
	(A) %	410	440	380	390	350	310	290	300	
Tensile Set	(W) %	20	15	23	30	29	7	2	1	
	(A) %	12	16	17	24	19	17	18	20	25
25 Trouser Tear	(W) kN/m	12.6	25.9	47.5	55.8	48.2	32.4	37.1	25.2	
	(A) kN/m	14.9	23.2	39.7	59.0	54.3	54.6	44.3	48.5	

Examples 5

- 30 Samples of polymer-fibre mixtures from Experiments 10–15 of Example 4 were mixed with further polymer of the same type used in Experiment 8 to provide final mixtures all containing 3 parts of fibre per hundred parts of polymer. This was done in duplicate using two different procedures. In the first procedure, the polymer-fibre mixture was banded on a two roll mill and the polymer slowly added, banded again, 3/4 cuts were made, 4 endwise passes were made and the product was finally sheeted off the mill. In the second procedure, the polymer-fibre mixture and the polymer were both added to a two roll mill, banded, 3/4 cuts made, 4 endwise passes were made and the product was finally sheeted off the mill.
- Examination of the final products showed them all to be uniform mixtures containing a few small agglomerations of fibres.

40

Example 6

- Latex samples of different polymers co-coagulated with fibre. The procedure used was that described in Example 3. For Experiment 16, the polymer was a butadiene-acrylonitrile polymer (about 34 weight per cent of acrylonitrile) in the latex form (about 26% solids), 100 ml of which was added to the coagulation vessel at a uniform rate over 14.6 minutes. The coagulation vessel contained 1 litre of 0.3 weight per cent solution in water of calcium chloride and was initially at 62°C, the temperature falling to 52°C at the end of the co-coagulation. The fibre (1.7 g) was suspended in 330 ml of water and was added in 10 ml portions over 13.5 minutes. The product was a small particle size crumb, was separated from the aqueous phase, washed and then dried in a hot air drier. Experiment 17 was a control, wherein the latex was similarly coagulated except that no fibre was added. The products of Experiments 16 and 17 were compounded (100 parts of polymer) with 50 parts of carbon black, 5 parts of di-octyl phthalate, 3 parts of zinc oxide, 1 part of stearic acid, 1.75 parts of sulphur, 1.5 parts of benzothiazyl disulphide and 0.5 parts of tetramethyl thiuram disulphide. Vulcanization was 4 minutes at 160°C. For experiment 18, the polymer was a styrene-butadiene polymer containing about 58 weight per cent of styrene in the latex form (about 27.3% solids), 100 ml of which was added to the coagulation vessel at a uniform rate over 14.6 minutes. The coagulation vessel contained 900 ml of a 4% solution of sodium chloride in water and 75 ml of the coagulant solution described in Example 3, and was at a temperature of about 55 to 50°C. The fibre (1.75 g) was suspended in 350 ml of water and was added in 10 ml aliquots over 13 minutes. The product was a small particle size crumb which was separated from the aqueous phase, washed and then dried. Experiment 19 was a control, wherein the latex was similarly coagulated except that no fibre was added. The products of Experiments 18 and 19 were compounded (70 parts of polymer) with 30 parts of styrene-butadiene polymer (about 23.5% of styrene), 30 parts of silica, 1 part of octylated diphenylamine, 5 parts of zinc oxide, 2 parts of diethylene glycol, 1

part of stearic acid, 1.5 parts of benxothiazyl disulphide, 0.3 parts of tetramethyl thiuram disulphide and 2.5 parts of sulphur. Vulcanization was for 10 minutes at 160°C. For Experiment 20, the polymer was a carboxylated butadiene-acrylonitrile polymer containing about 29% of acrylonitrile and about 7% of carboxylic acid in the latex form (about 26.1% solids), 100 ml of which was added to the coagulation vessel at a uniform rate over 15 minutes.

The coagulation vessel contained 1000 ml of a 6% solution of sodium chloride, sufficient sulphuric acid was added to maintain the pH at 2.5 and was at a temperature of about 50°C. The fibre (1.66 g) was suspended in 320 ml of water also containing 18 g of sodium chloride and was added in 10 ml aliquots over 14 minutes. The products was separated from the aqueous phase, washed with water and then dried. Experiment 21 was a control, wherein the latex was similarly coagulated except that no fibre was added. The products of Experiments 20 and 21 were compounded (95 parts of polymer) with 50 parts of carbon black, 1 part of stearic acid, 1.5 parts of tetramethyl thiuram disulphide, 1.5 parts of sulphur and 10 parts of a 50/50 masterbatch of butadiene-acrylonitrile polymer and zinc oxide. Vulcanization was for 9.5 minutes at 160°C. The results are shown in Table III.

TABLE III

Experiment		16	17	18	19	20	21
Fibre content of		3	0	3	0	3	0
20 polymer-fibre mixture phr							
Compound Green Strength							
Max. Stress	(W)MPa	1.9	—	5.6	3.5	5.1	1.3
	(A) MPa	0.8	0.5	3.4	3.4	1.3	1.1
Elongation	(W)MPa	110	—	65	90	150	>1500
25	(A) MPa	285	565	75	80	>1500	>1500
Vulcanizate Properties							
100% Modulus	(W)MPa	8.9	3.2	10.7	7.6	13.9	10.7
	(A) MPa	7.3	3.2	7.9	7.1	7.1	8.3
300% Modulus	(W)MPa	16.1	16.1	—	14.5	23.1	26.9
30	(A) MPa	16.1	15.9	14.2	13.7	21.3	25.4
Tensile Strength	(W)MPa	18.2	23.5	11.5	17.3	23.6	26.7
	(A) MPa	17.7	21.9	14.8	15.9	22.1	26.1
Elongation	(W)%	370	450	160	350	310	300
	(A) %	360	430	310	340	320	310
35 Tensile Set	(W)%	4	5	53	116	6	5
	(A) %	4	4	105	110	6	5
Trouser Tear	(W)kN/m	22.4	9.8	13.2	10.5	17.2	6.8
	(A) kN/m	21.2	8.9	13.8	13.8	18.5	8.7

40 Example 7

A sample of a polychloroprene latex (Neoprene Latex 102) was co-coagulated with fibre. 1.45 g of fibre was suspended with agitation in an aqueous solution of 400 ml water, 4 g of alum, 20 g sodium chloride and 75 ml of the coagulant solution described in Example 3, which was maintained at about 60°C. 50 ml of the latex (45.6% solids) was slowly added to the agitated mixture resulting in the formation of a small particle size crumb of polymer plus fibre which was separated, washed with water until the wash water had a pH of about 7 and air dried. This was labelled as Experiment 22. A control coagulation was also undertaken with no fibre present as Experiment #23. The polymers were compounded (based on 100 parts of polymer) with 40 parts of carbon black, 4 parts of magnesium oxide and 5 parts of zinc oxide. Vulcanization was for 20 minutes at 160°C. The results are shown in Table IV.

TABLE IV		22	23	
Experiment	Fibre content of			
5	polymer-fibre mixture phr			5
	Compound Green Strength			
	Max. Stress (W) MPa	6.2	4.4	
	(A) MPa	5.9	—	
	Elongation (W) MPa	105	155	
10	(A) MPa	145	—	10
	Vulcanizate Properties			
	100% Modulus (W) MPa	16.4	15.9	
	(A) MPa	15.5	12.8	
	Tensile Strength (W) MPa	19.0	21.3	
15	(A) MPa	18.6	18.9	15
	Elongation (W) %	120	125	
	(A) %	110	130	
	Tensile Set (W) %	0	0	
	(A) %	0	0	
20	Trouser Tear (W) kN/m	3.9	3.8	20
	(A) kN/m	4.2	4.0	

Example 8

- 25 A fibre dispersion was prepared by dissolving 7.5 parts by weight of calcium chloride in 1500 parts by weight of water and adding, with mild agitation, 10.4 parts by weight of the fibre of Example 1. The dispersion was then subjected to agitation for 20 seconds in a lab mixer. A sample of butadiene-acrylonitrile polymer latex (about 34 weight per cent of bound acrylonitrile) was prepared by adding 100 parts by weight of water to 38.5 parts by weight of a latex which contained about 10 parts by weight of polymer. The latex was then slowly added to the fibre dispersion with agitation. The polymer coagulated and physically covered the fibre. The product was separated from the aqueous phase, washed and recovered and yielded a polymer-fibre mixture which contained about 104 parts of fibre per 100 parts of polymer.

- 30 A sample (1 part by weight) of this polymer-fibre mixture was mixed on a rubber mill with 10 parts by weight of a butadiene-acrylonitrile polymer (about 34 weight per cent of bound acrylonitrile) and after about 15 minutes of mixing yielded a product containing an essentially uniform dispersion of fibre in polymer (i.e. about 0.5 parts of fibre in about 10.5 parts of polymer), which shows that the concentrated (in fibre) polymer-fibre mixture can be used to provide an essentially uniform mixture of a lesser proportion of the fibre in polymer.

Example 9

- 40 A fibre dispersion was prepared as in Example 8. A sample of styrene-butadiene polymer latex (about 23 weight per cent of bound styrene) was prepared by adding 100 parts by weight of water to about 46 parts by weight of a latex which contained about 10 parts by weight of polymer. The latex was then slowly added to the fibre dispersion with agitation and the coagulated polymer-fibre mixture was separated, washed and dried to yield a polymer-fibre mixture which contained about 104 parts of fibre per 100 parts of polymer.

- 45 Samples of the polymer-fibre mixture were mixed, separately, on a rubber mill or in a lab-sized internal mixer with further styrene-butadiene polymer or with polybutadiene and produced, after aqueous mixing time, essentially uniform dispersions of fibre in polymer.

CLAIMS

1. A process for the production of a mixture of a polymer and a fibrous material, which comprises agitating an aqueous solution of a coagulant for the polymer; adding an aqueous suspension of the fibrous material to the coagulant solution; adding the polymer, in aqueous latex form, to the coagulant solution; co-coagulating the polymer and the fibrous material; and recovering and drying the mixture of polymer and fibrous material.

2. A process according to claim 1, wherein the fibrous material is a polymeric paraphenylene terephthalamide aramid having an average fibre length of from 1 to 5 mm and a BET surface area greater than 1 m²/g.

3. A process according to claim 2, wherein the fibrous material comprises aramid fibres, used in the wet pulp form, and having a BET surface area of from 7 to 12 m²/g.

4. A process according to any preceding claim, wherein the polymer is a synthetic rubbery polymer.

5. A process according to claim 4, wherein the synthetic rubbery polymer is produced by

emulsion polymerisation and is selected from styrene-butadiene polymers, butadiene-acrylonitrile polymers, carboxylated styrene-butadiene polymers, carboxylated butadiene-acrylonitrile polymers, polymers comprising chloroprene and polymers comprising acrylic monomers.

- 5 6. A process according to claim 4, wherein the synthetic rubbery polymer is selected from butyl rubber, halogenated butyl rubber, polybutadiene and ethylene-propylene-non-conjugated diene polymers. 5
7. A process according to any preceding claim, wherein the mixture comprises from 0.25 to 100 parts by weight of the fibrous material per 100 parts by weight of the polymer.
- 10 8. A process according to any preceding claim, wherein the mixture comprises from 0.25 to 20 parts by weight of the fibrous material per 100 parts by weight of the polymer. 10
9. A process according to any preceding claim, wherein the aqueous latex contains from 10 to 45% by weight of the polymer, and wherein the coagulant solution is maintained at from 25 to 80 C during the coagulation.
- 15 10. A process according to claim 8, wherein the polymer is a styrene-butadiene or acrylonitrile-butadiene polymer or a polymer comprising chloroprene, and the coagulant solution is maintained at from 25 to 80 C during the coagulation. 15
11. A process according to any preceding claim, wherein part of the suspension of fibrous material is present in the coagulant solution before any latex is added.
- 20 12. A process according to claim 11, wherein the co-coagulation is a continuous process in which the suspension of fibrous material is added continuously or intermittently to the coagulant solution while the latex is being added. 20
13. A process according to claim 1, substantially as described in any of Experiment 3, Example 2, Experiments 4 to 7, 9 to 16, 18, 20, 22, Example 8 and Example 9.
- 25 14. A vulcanisation process which comprises mixing the product of a process according to any preceding claim with rubber-compounding ingredients and vulcanisation-active agents, shaping the mixture and vulcanising the shaped mixture at elevated temperature. 25

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1984, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.